

Molecular orientation in self-assembled multilayers measured by Second Harmonic generation using femtosecond pulses.

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Abstract: We present measurements of the optical second-harmonic generation in self assembled multilayer films of PAZO/PAH polymers with the aim to investigate molecular order in the layer-by-layer architecture. The experiments are performed in transmission, using a femtosecond Ti:Sa pulsed laser, which allows a more accurate determination of the amplitude of the second harmonic signal, without interference fringes usually present in nanosecond experiments. We found that the first bilayer, in contact with the substrate, presents a broad distribution of the orientation of the molecules, while the addition of successive bilayers (up to 12) produces ordering of the molecules with a small tilt angle respect to the surface normal. This result, together with the monotonic increment of the second harmonic signal with the number of layers indicates that the molecules grow orderly assembled in these films.

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1. Introduction

The ionic assembly as a route to make multilayered films was exploited widely, and different proposals to build well controlled films were reported [1]. In short, the alternate immersion of a charged substrate in solutions of anionic and cationic polyelectrolytes ends up in a self assembled film, mainly due to the electrostatic force between molecules of opposite charge. Among an enormous variety of applications of these films, one of the most important is the development of new nonlinear optical (NLO) materials. Films deposited layer-by-layer may exhibit second order NLO properties if one of the polyelectrolytes contains a chromophore oriented in a non centrosymmetric bulk assembly. Thick NLO films on the order of one micron were recently introduced [2], showing that a uniform growth can be obtained beyond the 500 bilayers. The influence of pH and ionic strength in layer formation was also pointed out in the literature, and substantial film thickness changes were observed under different pH conditions of the polyanion and the polycation [3,4]. On the other hand, one question still remains regarding the ordering of these types of layered materials, for which the presence of the chromophore may perturb the intrinsic organization of the film. Optical Second Harmonic (SH) generation has proven to be an excellent tool to test the growth as well as the microscopic organization of multilayer polymer films, although it is not addressed as often as the more traditional UV/VIS spectroscopy or ellipsometry techniques. In particular, the study of the polarization properties of the SH signal provides a direct measurement of the average molecular orientation in mono- and multi- layers [5,6], constituting an invaluable information that can not be achieved by other techniques. However, and restricted only to the films build with azo-functionalized polyanions, there are contradictory reports in the literature showing in some cases a continuous increment of the SH signal [2,4,7,8], which renders in a continuous ordered growth, or a saturation or drop off of the SH [9], interpreted as a collapse or disorder of the film after a given number of layers. Also, discrepancies arise in the determination of the molecular tilt angle due to the effect introduced by the width of the distribution [6]. Almost in the hundred percent of the cases, picosecond or nanosecond pulsed lasers are chosen for SH measurements, mainly Nd:YAG lasers with mJ of energy per pulse. Interference fringes, not related with the molecular orientational information but with the film growth in both sides of the substrate, appear in the SH signal due to the longer coherence length of Nd:YAG lasers compared to the size of the substrates [10]. Although the fringes are fully understood and resemble the very well known Maker fringes [11], femtosecond experiments appear free from those fringes, which may result in the improvement of the quality of the information retrieval. Here, we present SH measurements of PAZO/PAH multilayer films up to 12 bilayers, taken with a Ti:Sapphire femtosecond laser and show that the films grow without collapsing and the orientation of the molecules tends to be a sharp distribution around the normal to the surface. Spectral photon counting detection gives SH signals of several thousands of counts per second, which are easily detectable and free of interference fringes.

1.1 Brief review of the Second Harmonic Generation in molecular films

SH signal comes from the nonlinear electronic susceptibility of materials, $\chi^{(i)}$. These higher order terms in the response of the material become evident in presence of intense external fields E , being the polarization:

$$P = \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \dots \quad (1)$$

At the microscopic level, the polarization can be described as a power series as well, where the term of interest for second harmonic generation is proportional to the molecular hyperpolarizability tensor $\beta^{(2)}$. While the $\chi^{(2)}$ tensor describes the second-order nonlinear response of the material, the $\beta^{(2)}$ tensor describes the SH response of an isolated chromophore.

$$p_i = \mu_i + \alpha_{ij}^{(1)} E_j + \beta_{ijk}^{(2)} E_j E_k + \dots \quad (2)$$

Every nonzero element of the macroscopic susceptibility tensor $\chi^{(2)}$ can be related to the NLO response of an isolated chromophore through orientational averages [12]. A parameter commonly used to express orientation is the so-called orientation parameter D [6]:

$$D = \frac{\langle \cos^3 \theta_{zz'} \rangle}{\langle \cos \theta_{zz'} \rangle}, \quad (3)$$

where $\theta_{zz'}$ is the tilt angle between the long molecular axis (z') and the surface normal (z), and the brackets indicate an average value. If the distribution about the mean orientation angle is narrow, then the average tilt angle of the chromophores away from the surface normal can be determined considering $D \cong \cos^2 \langle \theta_{zz'} \rangle$. For rod-like chromophores (i.e., for molecules with a dominant second-order $\beta_{zz'z'}$ molecular nonlinear polarizability tensor element) specific relations [12] between the elements of $\chi^{(2)}$ and orientation averages gives:

$$D = \frac{\chi_{zzz}^{(2)}}{\chi_{zzz}^{(2)} + 2\chi_{zxx}^{(2)}}. \quad (4)$$

Therefore, to determine the angle $\theta_{zz'}$, one should extract the value of the second-order NLO tensor $\chi^{(2)}$ from the SH experiment and replace it in (4). The nonzero elements of $\chi^{(2)}$ can be evaluated from the SH intensities polarized parallel (p) or perpendicular (s) to the plane of incidence, as a function of the polarization of the fundamental beam. For a system with a single unique axis (typical of most thin organic film systems), only three of the possible 27 elements of the $\chi^{(2)}$ tensor are nonzero; namely, χ_{zzz} , $\chi_{zxx} = \chi_{zyy}$ and $\chi_{xxz} = \chi_{xzx} = \chi_{yyz} = \chi_{yzy}$. If one assumes that the surface layer thickness d is much smaller than the wavelength of the SH, then the specific relationship between the transmitted s - and p -polarized SH intensities and the $\chi^{(2)}$ tensor elements is given by [13]

$$I_s^{2\omega}(\gamma) = C d^2 |s_1 \sin(2\gamma) \chi_{xxz}|^2 (I^\omega)^2, \quad (5a)$$

$$I_p^{2\omega}(\gamma) = C d^2 |\cos^2(\gamma) [s_2 \chi_{xxz} + s_3 \chi_{zxx} + s_4 \chi_{zzz}] + s_5 \chi_{zxx}|^2 (I^\omega)^2, \quad (5b)$$

where $I^{2\omega}$ is the SH intensity, the subscripts indicate the polarization, I^ω is the intensity of the incident beam, γ is the polarization angle of the fundamental beam ($\gamma = 0^\circ$ corresponds to p -polarized light), C is the instrument response, and s_n are coefficients dependent on the angle of incidence, θ_i , and linear and nonlinear Fresnel factors [13,14].

The refractive index of the polymer film and the substrate at ω and 2ω defines the position of the maximum of $I^{2\omega}$ when plotted as a function of θ_i , through the Fresnel factor dependence on these parameters. Reasonable values for the refractive indexes give the angle at the maximum between 60 to 80 degrees [13,14]. Transmission experiments have the advantage that measurements as a function of the incident angle are simpler to perform, compared to reflection experiments. However, signal becomes more complex when the SH signal generated from one side of the substrate interferes with the SH generated at the other side [10]. In these cases, equation (5) describes only the envelope, although the detected signal is modulated by interference fringes. Fringes appear if the coherence length of the laser is larger than the width of the substrate, which is on the order of 150 μm for a coverslip and 1 mm for a microscope slide. Nanosecond lasers have typically tens of centimeters of coherence length while femtosecond lasers have only few microns, justifying why there are no fringes in our

experiment. In this paper we measure always at the incident angle of the maximum signal, adjusting the focus of the beam if necessary.

2. Experiment

2.1 Multilayer fabrication

Poly(allyl-amine) (PAH, Aldrich) and Poly [1-[4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfo-namido]-1,2 ethanediyl] sodium salt (PAZO, Aldrich) were dissolved in water at appropriate concentrations (10 mM monomer, PAH pH 5.5, PAZO pH 7.6). All solutions were prepared with 18 mΩ Milli-Q (Millipore) water. Films for SH experiments were grown on glass slides of 0.1 cm width, previously sonicated for 20 min with 60% ethanol + 39% water + 1% KOH at 50°C and then rinsed with water. Layer-by-layer self-assembled films were obtained by dipping the substrate alternately in solutions of both PAH and PAZO, oppositely charged polyelectrolytes. Freshly cleaned glass substrates bearing negative surface charge were first immersed in PAH solution for 10 min to adsorb a layer of PAH, followed by rinsing with water. The positively charged PAH layer allows the deposition of the next layer of PAZO. The substrates were then immersed in the PAZO solution for 10 min to adsorb the following layer, and again rinsed with water. By repeating the above steps, films of multiple bilayers (PAH/PAZO)_n (*n* refers to the number of deposition cycles) have been prepared. We monitored the assembly process by UV/VIS absorption spectroscopy (Shimadzu UV-1603 spectrophotometer). The thickness of the films was measured by ellipsometry (Sentech SE400 ellipsometer). Measurements were performed at an incident angle of 70.00° and with a 632.8 nm laser as the polarized light source.

2.2 SH measurements

The experiments were performed in transmission, using a modelocked Ti:Sa laser (50 fs pulse width, 400 mW average power, 80MHz repetition rate, 780-800 nm) focused by a glass lens (2.5cm focal length) down to a spot size of about 5μm diameter. Transmission polarized or unpolarized signal enters into a monochromator (Metrolab 250AA), after which the SH is detected by a photomultiplier tube (Hamamatsu 1P28) with photon counting sensitivity. The polarization response of the monochromator has been taken into account. The samples were rotated around an axis parallel to the optical table to adjust the angle of incidence.

3. Results and discussion

3.1 Characterization of Multilayer Films

UV/VIS absorption spectra of films with different number of layers are shown in Fig. 1(a). All spectra have the absorption peak at 370 nm, which is attributed to the absorption of PAZO.

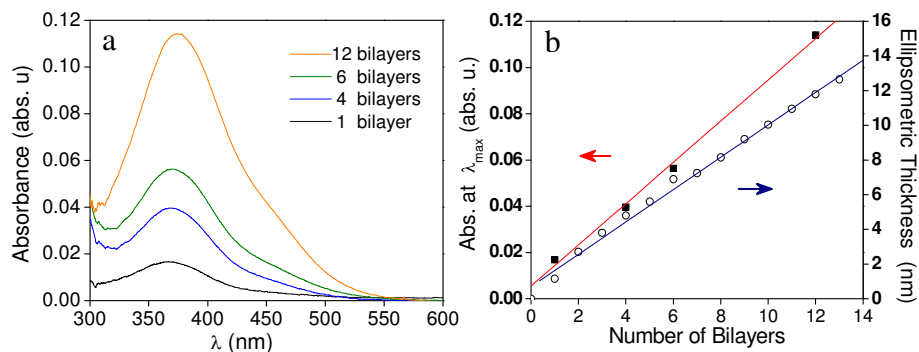


Fig. 1. (a) UV/Vis spectra of the (PAH/PAZO)_n assemblies. Curves, from down to top, correspond to *n* = 1, 4, 6, and 12. (b) Absorbance at the maximum (black squares) and ellipsometric thickness (open circles) as a function of *n*, solid lines are linear fits. The thickness increases about 1 nm per bilayer.

The linear increase of the absorbance at this wavelength (Fig. 1(b)) with the number of deposited bilayers confirms that an equal amount of PAZO was adsorbed in each deposition cycle. The absorption peak of the azobenzene chromophore showed a considerable red-shift in the film as compared to that in water solution. Formation of J-aggregates of azobenzene chromophores has been suggested to be responsible for the observed red-shift [8,9]. The linear growth of the films is also confirmed by the thickness dependence on the number of bilayers, shown in Fig. 1(b). A refractive index of 1.51 was obtained for the films from these ellipsometry measurements.

3.2 Second Harmonic Generation

Figure 2(a) shows a typical SH spectrum obtained for a multilayer (PAH/PAZO)₁₂ film, taken at the γ that maximizes the signal. The peak intensity corresponds to half of the incident wavelength. Note that the signal, even after the monochromator, is well beyond the thousand of counts per second, while the background signal is below a hundred of counts. Spectrum and power dependence of the SH intensity is always checked, as in Fig. 2(b) which shows the quadratic increment of the SH at the maximum as a function of the input power.

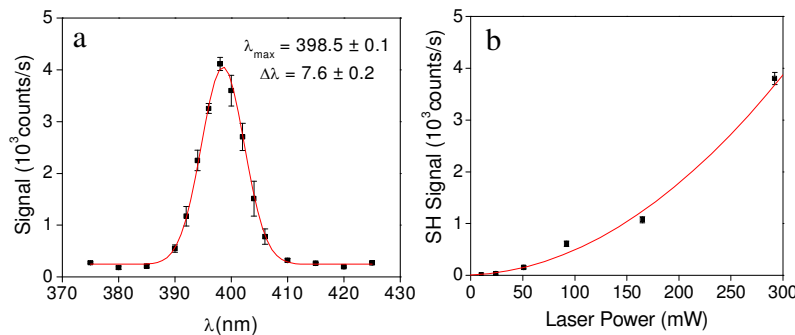


Fig. 2. (a) Spectral response of (PAH/PAZO)₁₂ film proves that the observed signal is SH. (b) Excitation power dependence of the SH signal at $\lambda_{2\omega} = 398$ nm, following a quadratic law.

3.3 Orientation measurements

By construction of our experimental setup, horizontal and vertical components of the signal respect to the lab system of coordinates, have a small rotation angle of 15 degrees respect to the p - or s - polarized components of the SH at the sample. Then, we call s' and p' the rotated coordinates. We measure the s' - and p' -polarized SH response for 1, 6, 9, and 12 bilayers films. As an example, Fig. 3 shows the dependence of the s' -, p' -polarized and total SH signal for of (PAH/PAZO)₆. Full lines in Fig. 3 are the fittings with Eq. (5) taking into account the setup rotation of 15 degrees. All the parameters used for the fits are taken from experimental values measured for these specific films (n , d and θ_i which, in turn, are used to calculate the s_n parameters for each measurement). The average chromophore orientation angles with respect to the substrate normal obtained are: 17° for the 1 bilayer film and 0° for films of 6, 9 and 12 bilayers, with an uncertainty of 3°.

It has been shown [6] that the assumption of a narrow distribution about the mean tilt angle (which made the calculation of this angle possible) is not always reliable, yielding an apparent tilt angle that may differ from the true distribution mean. Moreover, in the limit of broad orientation distributions, the orientation angle converges to an apparent tilt angle of about 39°, which is called the SH magic angle. Apparent angles close to the SH magic angle can be obtained for two very different distributions: a narrow distribution about the magic angle, or a broad distribution about an arbitrary unknown angle. In our results for 6, 9 and 12 bilayers we found a 0° tilt angle, indicating that in those films the molecules are orientated normal to the surface. Since 0° is far from the magic angle we, therefore, conclude that it can be only obtained for a narrow distribution. On the other hand, considering previous results [6],

an angle of 17° , as the one we obtained for the first bilayer film, can be obtained from a narrow distribution about a 17° or from a broad distribution about a smaller angle. It is likely that, as being in contact with the substrate, the chromophores have a broad distribution in the first bilayer (possibly due to substrate roughness) and became ordered in an angle almost normal to the surface as the number of bilayers increases.

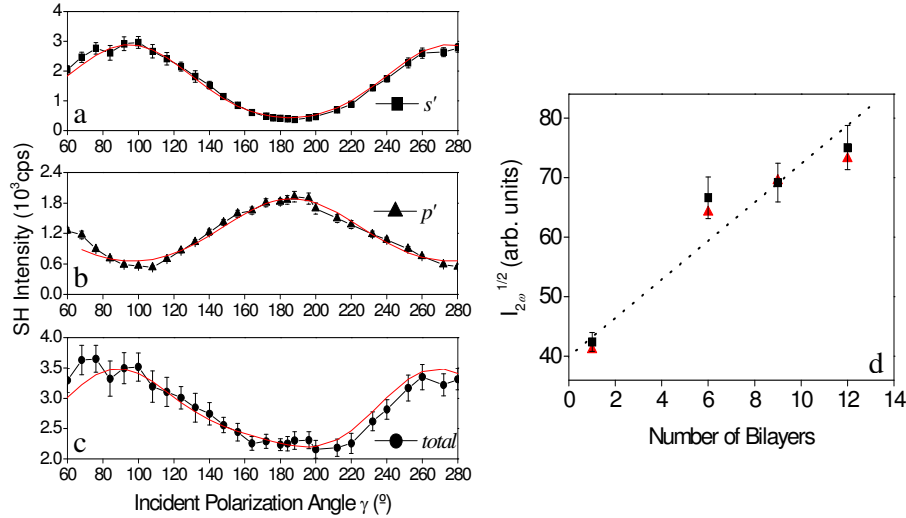


Fig. 3. (a) s' - and (b) p' -polarized SH response (rotated 15 degrees from the s - or p - polarized signals) of (PAH/PAZO)₆ as a function of the polarization angle of the fundamental beam (90° corresponds to s - polarized incident beam). (c) is the total signal. Full lines are fittings following Eq (5). (d) Square root of second-harmonic intensity of PAH/PAZO films as a function of the number of deposited bilayers. Squares correspond to the maximum total signal measured, triangles correspond to the same quantity obtained from the fitting function. Dotted line is a guide to the eye.

Figure 3(d) shows the relationship between the square root of the SH signal (considered as the maximum of the total signal, Fig. 3(c)) and n , in which a monotonic increment of the signal can be seen. As expected from equation (5), the signal should be quadratic with n if (i) d is proportional to n and (ii) χ_{iii} are constant along the bilayers. Even assuming that d is proportional to n , we do not expect an exact quadratic behavior, since the distribution width has been shown to be broader for the first bilayer and, therefore, the χ_{iii} values may change from the first to the subsequent bilayers. The increment of the SH indicates that the chromophores are not disordered even for a higher number of bilayers, and that the film grows regularly along. This assumption reinforces the results obtained for the polarization dependence measurements.

4. Conclusions

In this paper we show that second harmonic measurements in self-assembled multilayers can be easily performed with non-amplified femtosecond pulses on the order of the nJ per pulse, avoiding interference fringes, which may increase the level of difficulty on the retrieval of the relevant information. We also show that PAH/PAZO films grow uniformly, and that the chromophores are oriented close to the surface normal up to the 12 bilayers tested. The presence of the chromophores does not perturb the ordered growth of the layer by layer architecture. The first bilayer copies somehow the roughness of the substrate giving an orientation angle compatible with a small angle and a broad distribution around it.

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